In-situ Solvothermal Synthesis of Novel High-Capacity Cathodes

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Brookhaven National Laboratory

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ES183

Overview

Timeline

- Start date: Oct., 2015
- End date: Oct., 2018
- Percent complete: 50%

Budget

- Total project funding
  - DOE 100%
- Funding received in FY 2015
  - 350K
- Funding for FY 2016
  - 350K

Barriers

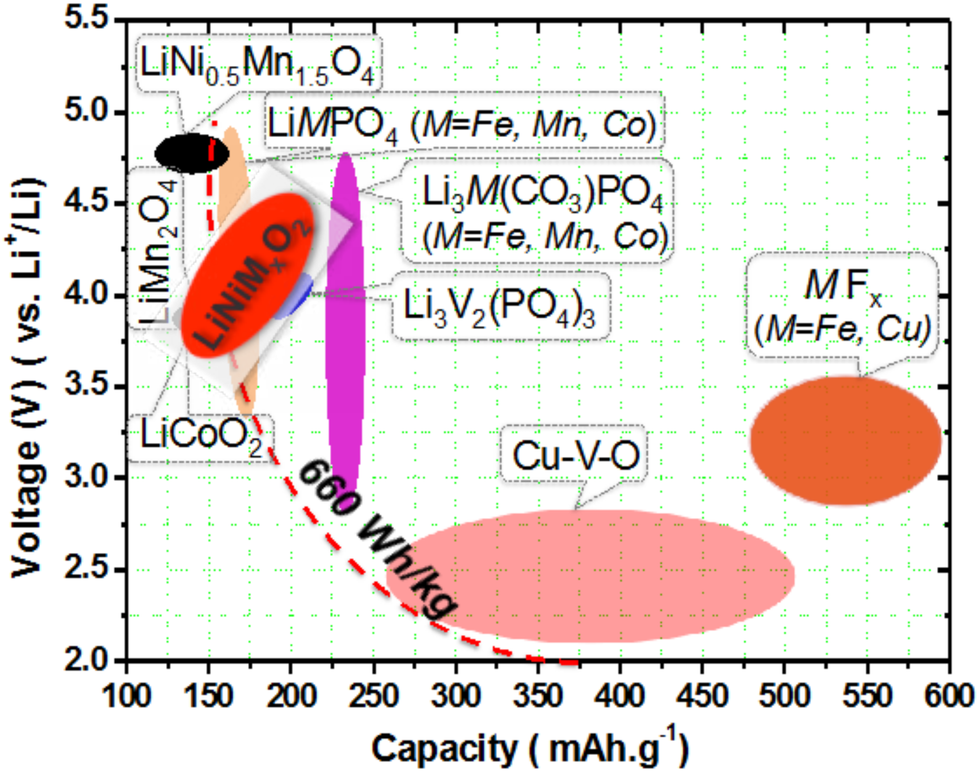
- Barriers addressed
  - Low energy density
  - Cost
  - Cycle life

Partners

- Interactions/collaborations
  - Lawrence Berkeley National Lab
  - Oak Ridge National Lab
  - Argonne National Lab
  - Stony Brook University
- Project lead
  - Brookhaven National Lab

Relevance and Objectives -

Develop *low-cost* cathode materials with *energy density >660 Wh/kg* and electrochemical properties (cycle life, power density, safety) consistent with USABC goals.



The effort in FY16-FY17 is focused on developing Ni-rich layered oxides

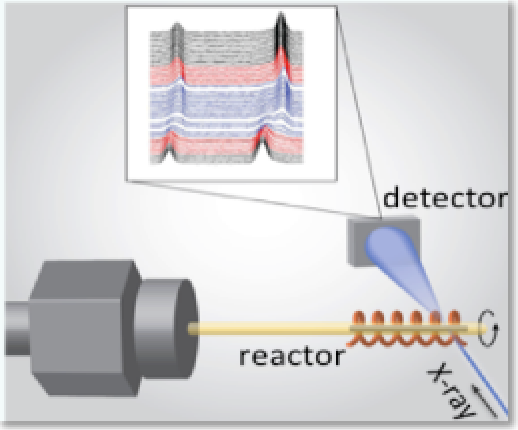
– $LiNi_{1-x}M_xO_2$ (M=Co, Mn, …)

through synthetic control of the phase, stoichiometry and morphology.

(**Some cathodes with target energy density (>660 Wh/kg) are given on the right side of the red dashed plot*)

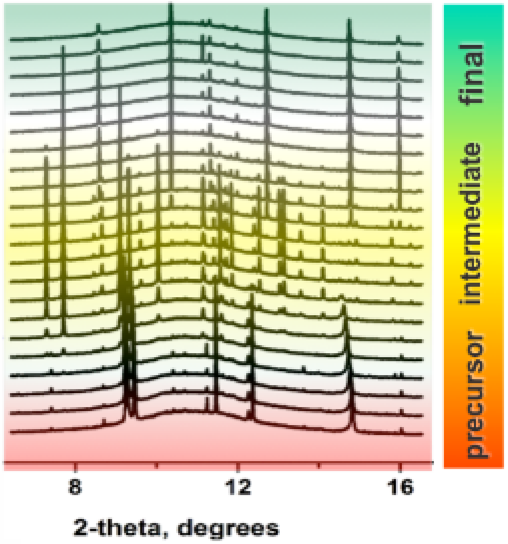
Approach: *Synthesis by Design*

Electrochemical performance of electrodes is often limited by the phases, stoichiometry and morphology of the active materials.



Cathode performance can be advanced by

- synthesis of phase-pure materials
- control of stoichiometry, morphology

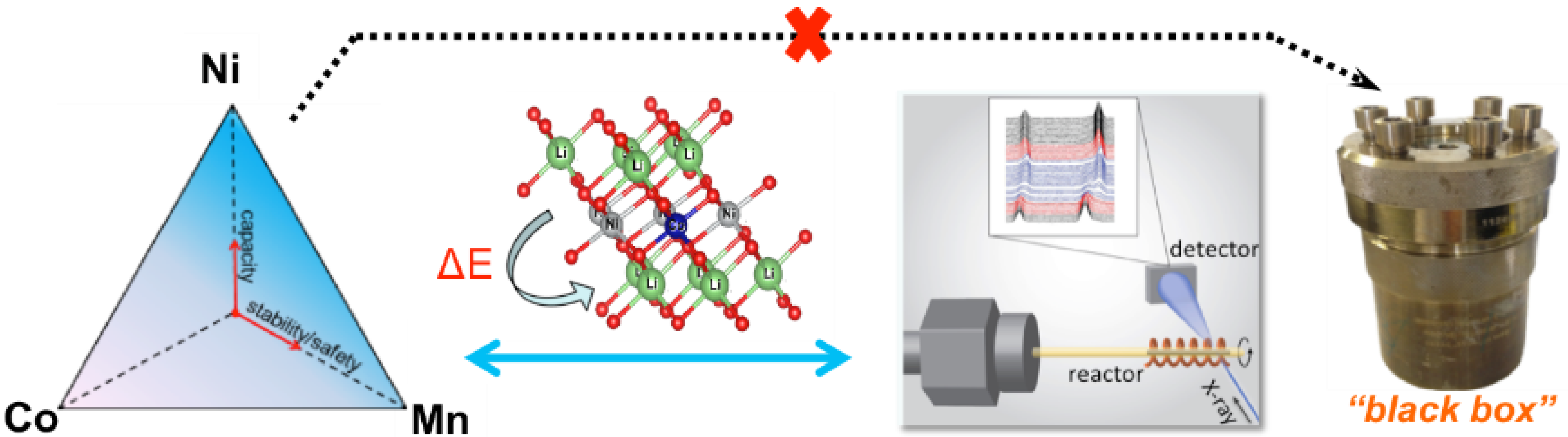


- Tools/techniques have been developed for *in-situ*, *real time* studies of synthesis reactions under real conditions, enabling us to identify the reaction pathways for making electrode materials of desired phases and properties.
  - Example: *in situ* solvothermal synthesis of $LiFePO_4$ (Bai *et al.*, J. Phys. Chem. C, 119 (2015) 2266)

Approach-*continued*: for developing Ni-rich layered oxides

$Li_{1-x}Ni_{1+x}O_2$: cation mixing/off stoichiometry (**among many other issues*)

$LiNi(MnCo)_xO_2$: tuning structure/property with Co, Mn substitution



Phase diagram ⇔ **Theory** ⇔ ***In-situ* studies** ⇔ **Synthesis**

Approach: synthetic control *via in-situ* probing synthesis reaction

- explore the "phase space" under real synthesis conditions
- track phases/cation ordering in the intermediates

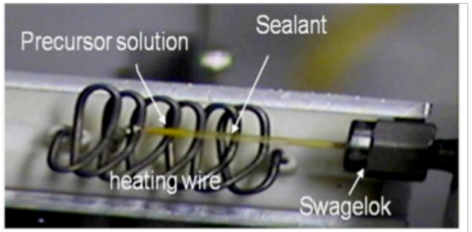
and thereby quantify thermodynamic and kinetic parameters governing synthesis process.

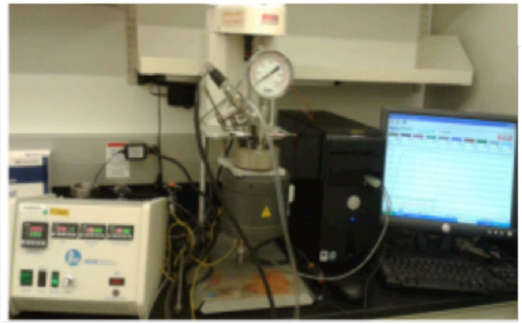
Milestones

Time	**Description (*status*)**
June, 2016	Develop new capabilities for monitoring synthesis parameters (*P, T, pH*) in real time during solvothermal synthesis of cathode materials (*complete*)
Sept., 2016	Identify synthetic approaches for stabilizing the layered structure of Ni-Mn-Co (NMC) cathodes. (*complete*)
Dec., 2016	Identify the synthesis reactions and associated structural ordering in both Ni- and Co-rich layered oxides through *in situ* synchrotron X-ray studies. (*complete*)
March, 2017	Develop neutron scattering-based techniques for *in situ* probing cation ordering in NMC layered oxides under real synthesis conditions. (*complete*)
June, 2017	Identify synthesis procedures for kinetic control of structural ordering in NMC layered oxides through combined *in-situ/ex-situ* synchrotron X-ray and neutron studies. (*on schedule*)

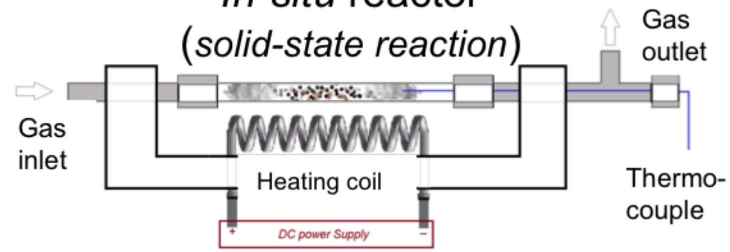
Accomplishment (1) Developed new reactors/capabilities: i) cover broad synthesis space; ii) enable quantitative measurements

In-situ reactor
(hydrothermal/*solvothermal*)

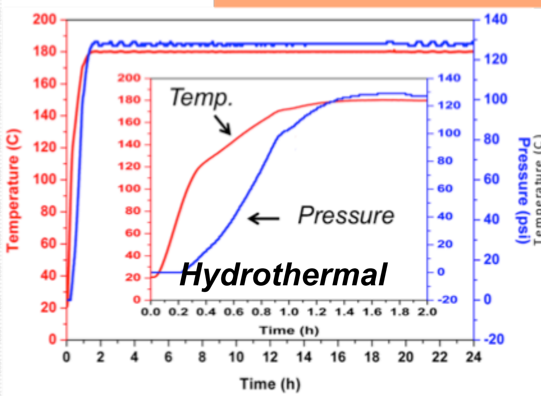


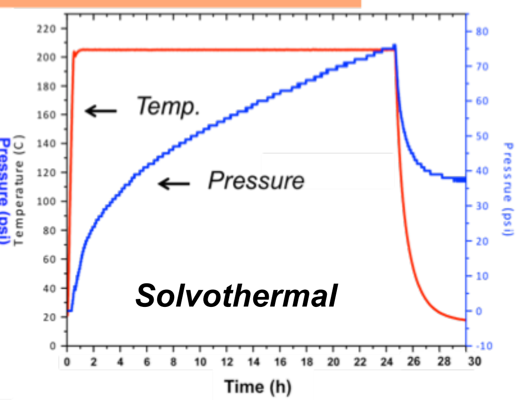


In-situ reactor
(*solid-state reaction*)

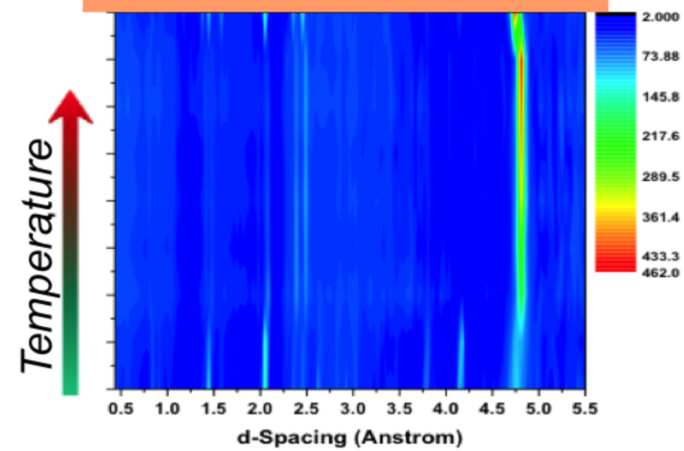


Online monitoring of (*T, P, pH*)



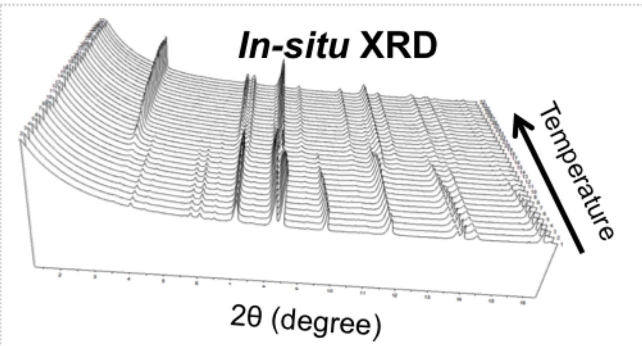


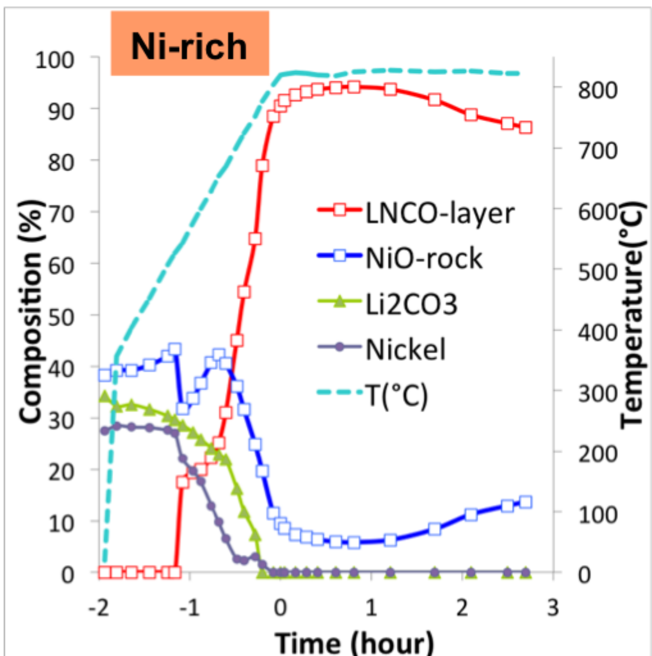
In-situ neutron diffraction

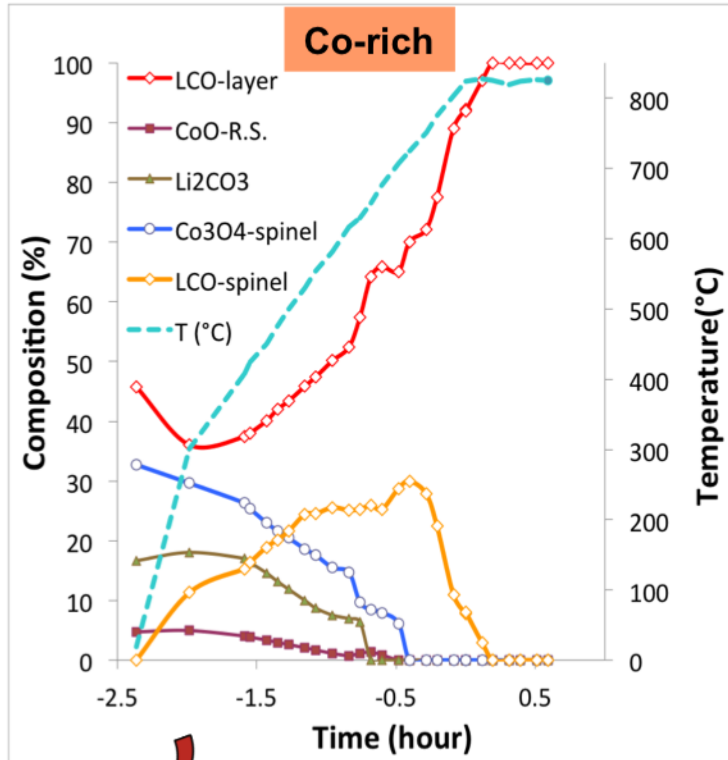


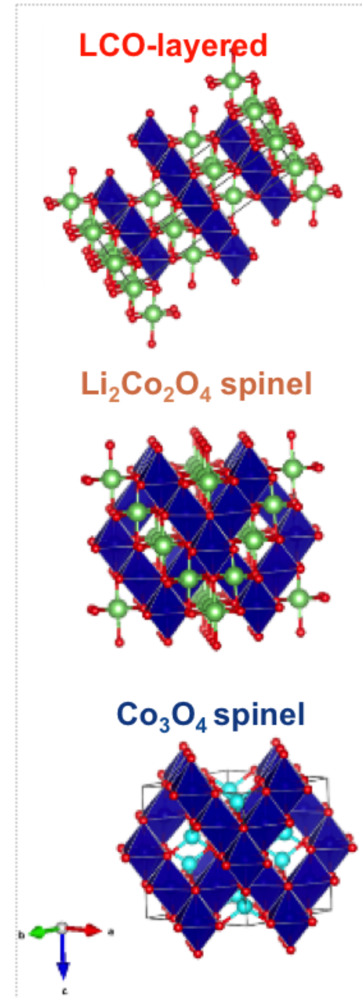
- Built a high temp./pressure autoclave system capable of monitoring *P, T, pH* online-- key parameters governing pathways of solvothermal reaction
- Designed *in-situ* reactors specialized for solid-state synthesis under controlled atmosphere
- Developed new synchrotron, neutron-based *in-situ* probing techniques

Accomplishment (2) Identified reaction pathways of forming layered/spinel composites in *Ni/Co-* rich systems, with tuned electrochemical properties (*Ref.*: *Eungje, et al. "Exploring Lithium-Cobalt-Nickel Oxide Spinel Electrodes for ≥ 3.5 V Li-Ion Cells." ACS Appl. Mater. Interfaces 8 (2016) 27720*).



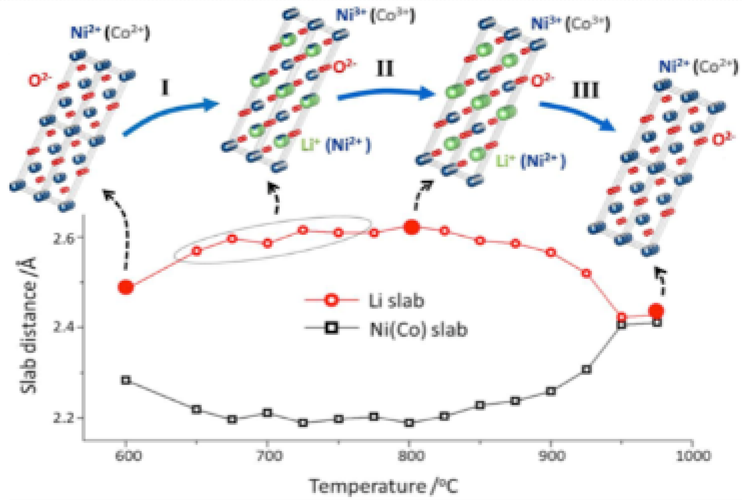


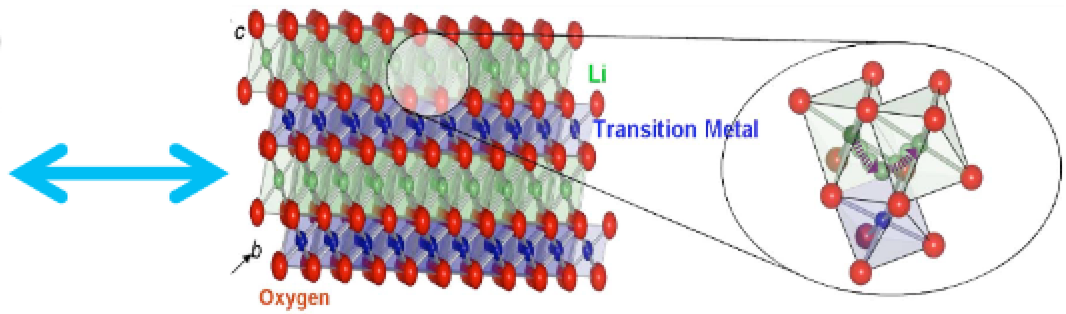




- **Ni-rich *vs* Co-rich systems**: different pathways resolved by *in-situ* studies

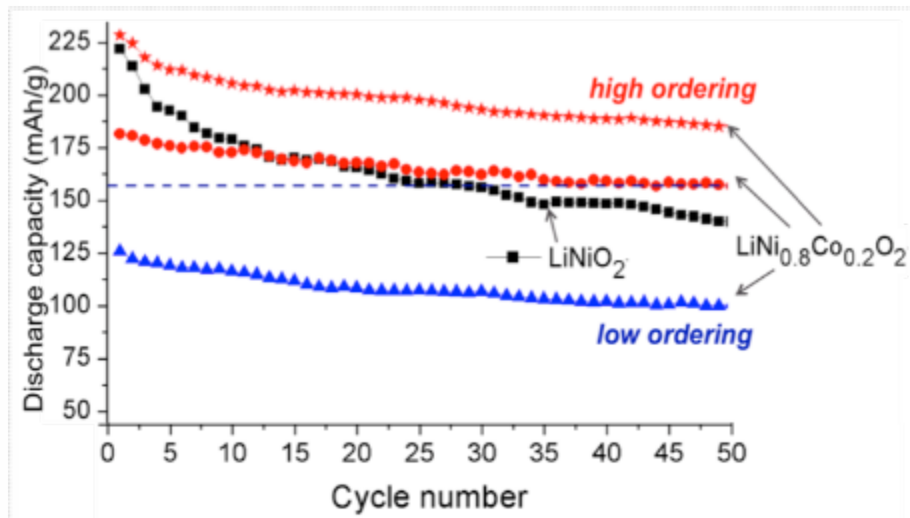
Accomplishment (3) Developed approaches for *in-situ* probing and synthetic control of structural/electrochemical properties in Ni-rich layered oxides ➔ *enabling high reversible capacity*.



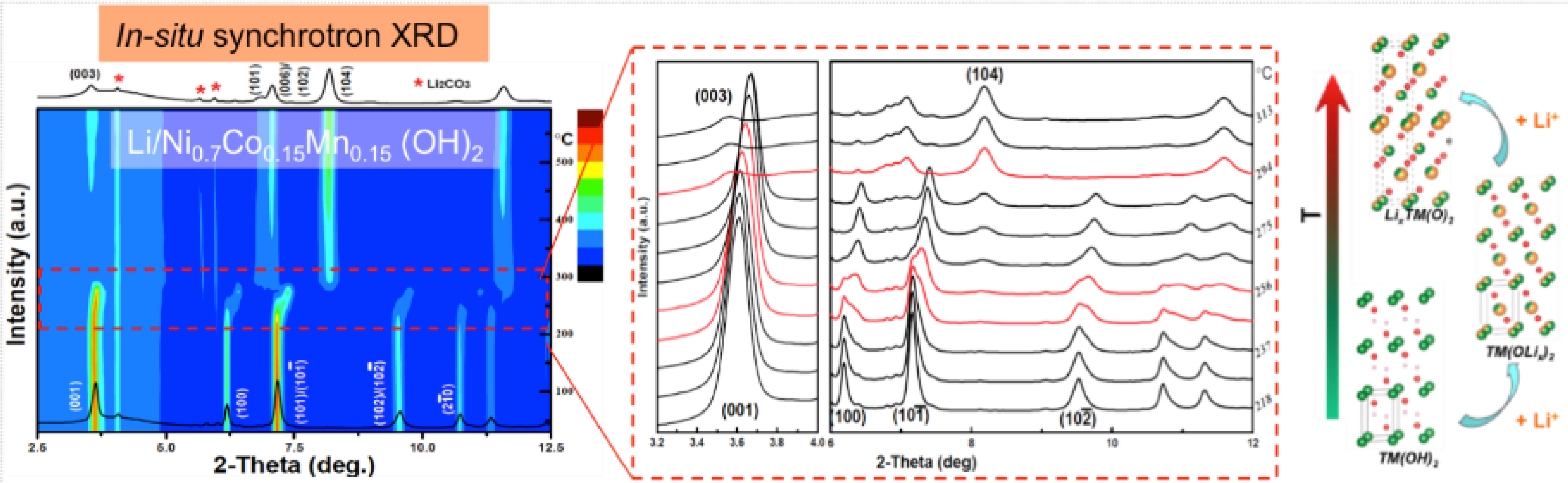


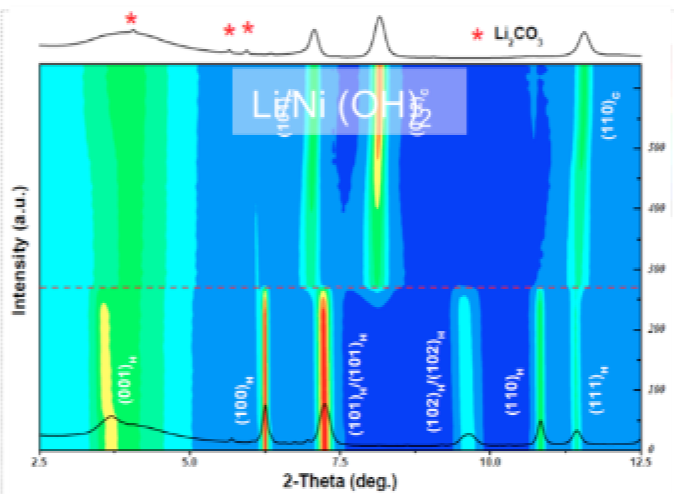
Li slab distance: electrochemical activity
(Kang, Ceder, Phys. Rev. B 74 (2006) 94105)

- Identified details of structural evolution with temperature during synthesis (phase transformation, layer ordering, Li/Ni mixing, slab distance)
- Determined optimal conditions for synthesizing $LiNi_{0.8}Co_{0.2}O_2$ with low cationic disordering.



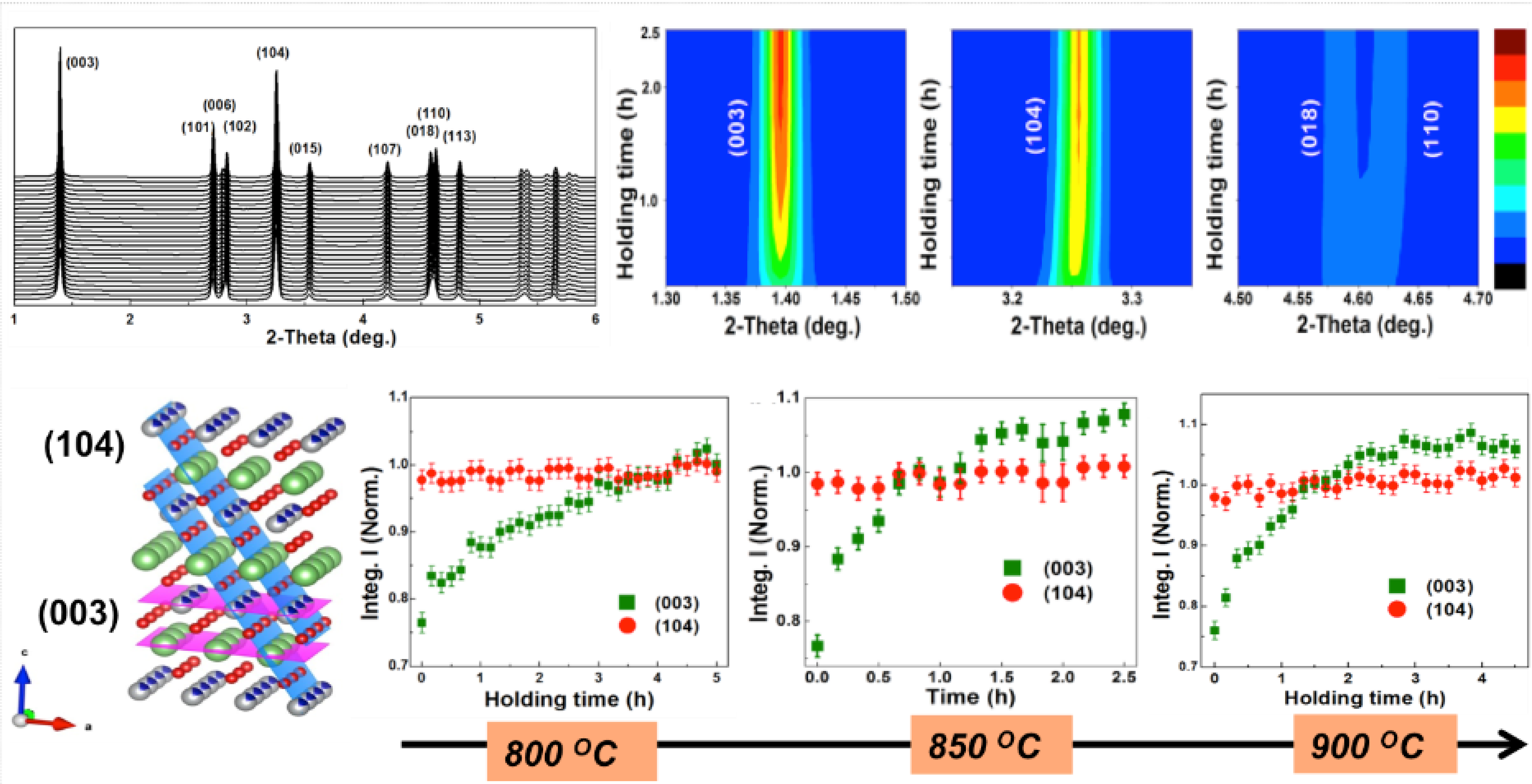
Accomplishment (4) Determined the dependence of reaction pathway on precursors in synthesis of Ni-rich layered oxides: *facilitated transformation from* hydroxide precursors *to the layered by Co/Mn.*



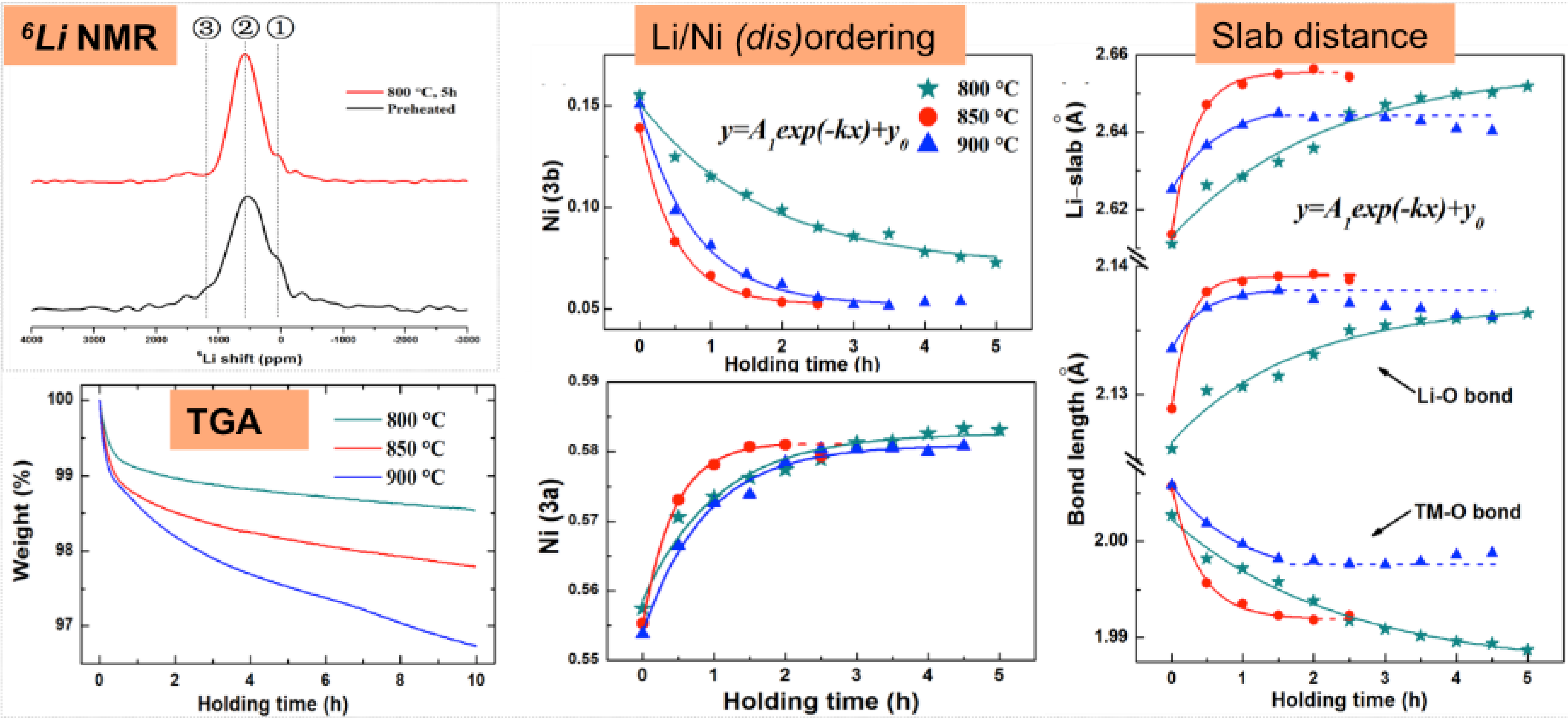


- **Precursor effects**: different pathways due to the presence of Co/Mn (*i.e.* $Ni(OH)_2$ *vs* $Ni_{0.7}Co_{0.15}Mn_{0.15}(OH)_2$);
- ➔ **quantitative analysis** *via* structure refinement of the *in-situ* XRD data, to resolve the details: complex process involving anionic/cationic exchange.

Accomplishment (5) Identified strong temperature dependence of the ordering kinetics in high-Ni layered oxides ($LiNi_{0.7}Mn_{0.15}Co_{0.15}O_2$; NMC71515), enabling synthetic control of the kinetic pathway for making layered oxides with high structural ordering.

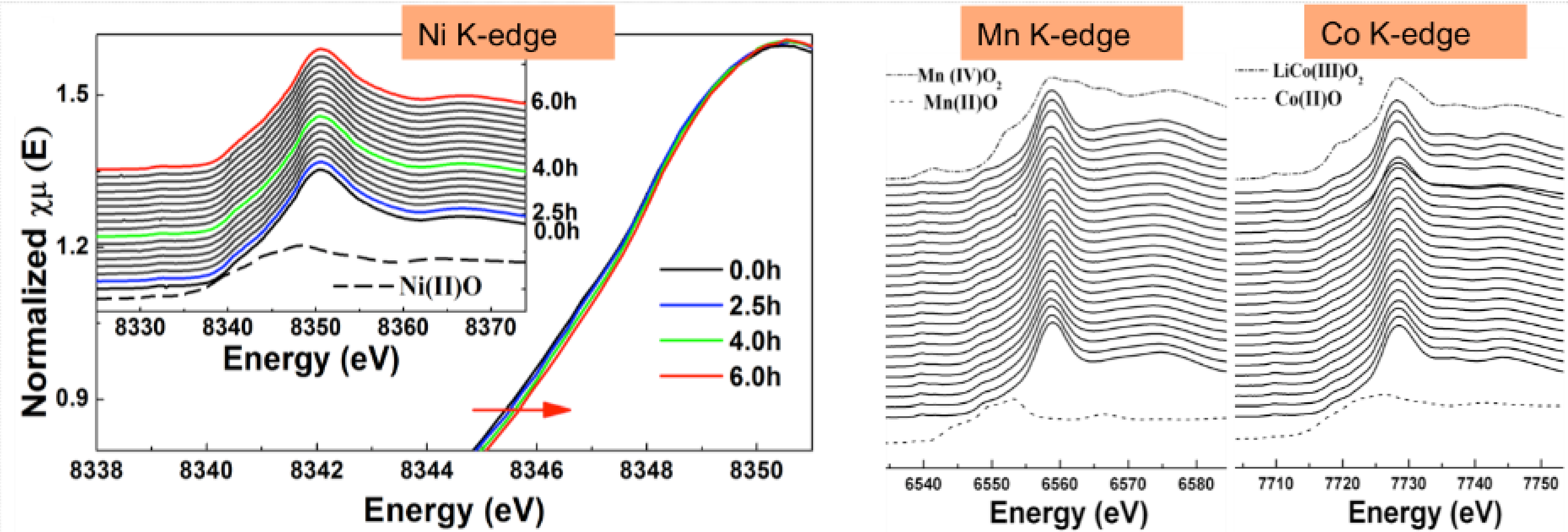


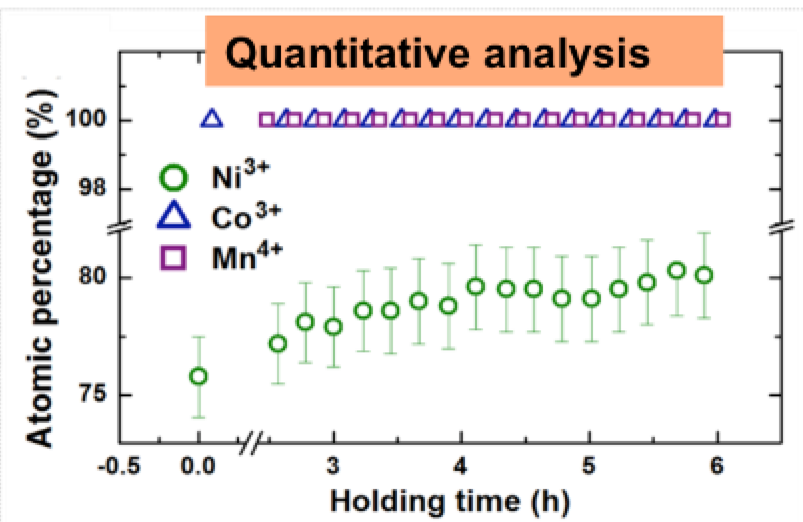
Accomplishment (5)-*continued* (quantitative structure analysis *via* refinement of *in-situ* XRD data, NMR, TGA)



- Identified cationic ordering process at different temperatures
  - fastest ordering kinetics at 850°C, in contrast to monotonic increase of mass loss with temperature (due to Li/O loss);
  - large Li-slab distance at 850°C ➔ high electrochemical activity.

Accomplishment (5)-*continued* (*in-situ* XAS studies)

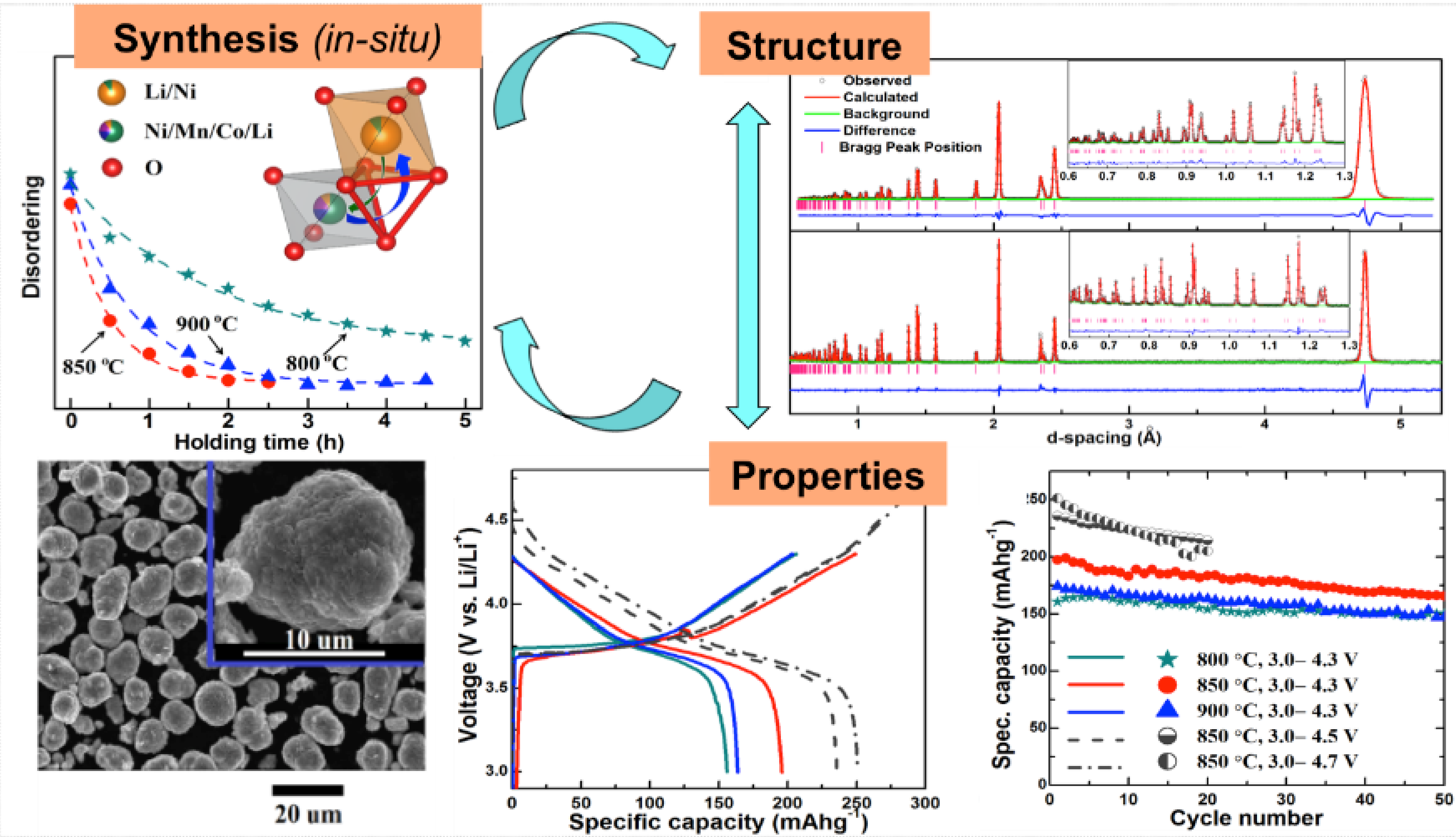




- Identified oxidation sequences of all constituent transition metal elements (Mn, Co Ni)

➔ unprecedented insights into the coupling of Ni oxidation with Li/Ni (dis)ordering in octahedral sites (*via combined in situ XAS/XRD analysis*)

Accomplishment (6) Synthesized NMC71515 with low cationic disordering and high reversible capacity, through synthetic control of the kinetic reaction pathway ➔ **opening a new avenue to prepare high performance Ni-rich layered oxides.**



Response to Reviewers' Comments

This project was not reviewed last year.

Collaborations

- **Brookhaven National Lab** (*J.P. Looney*, *L. Wu, Y. Zhu*)
  - *Techniques/capabilities for synthesis and characterization of new cathodes*
  - *Advanced TEM imaging and spectroscopy of cathodes*
- **Argonne National Lab** (*Z. Chen, Y. Ren, C. Sun, K. Amine*)
  - *Precursors for preparing Ni-rich layered oxides*
  - *In-situ synthesis and characterization of Ni-rich layered cathodes*
- **Lawrence Berkeley National Lab** (G. Ceder, *N. Balsara, W. Tong*)
  - Theoretical prediction of the phases/ordering in Ni-rich layered cathodes
  - Synthesis and characterization of cathode materials
- **Oak Ridge National Lab** (*J. Nanda, A. Huq*)
  - *Neutron/synchrotron characterization of Ni-rich layered cathodes*
- **Xiamen U.** (*Y. Yang*)
  - *Surface treatment and characterization of layered cathodes for working at high voltages*
  - *Develop high-voltage polyanionic cathodes*
- **Alfred U.** (S. Misture)
  - *In-situ synthesis and characterization of Ni-rich layered cathodes*
- **Stony Brook U.** (*E. Takeuchi, P. Khalifah*)
  - *Synthesis of new high-capacity cathodes*
- **Seoul Nat. U.** (*K. Kang*)
  - *Synthesis of new high-capacity cathodes*

Remaining Challenges and Barriers

- **Main barrier:** general principles have been established for designing cathode materials, but so far there has been no theory or design principles on synthesizing materials of desired structure/properties: *we know what we want but don't know how to make them.*
- **Technical challenge**: designing and synthesizing specific cathode materials has proven difficult due to the complexity of the reactions involved in chemical synthesis, and high sensitivity of the phases, stoichiometry and morphology to the synthesis conditions (such as *pH value*, *Li content*, *sintering temperature/atmosphere*, *heating/cooling rates*…)
  - synthesis of Ni-rich layered oxides is even more challenging, due to the demanding requirement on the synthetic control of the cationic disordering and surface rock-salt layer (*both being detrimental to the electrochemical performance*).

Future Work (2017)

- Continue to work on *in-situ* probing and synthetic control of the structural ordering in NMC cathodes, with focuses on
  - Co and Mn effects on the structural ordering
  - cooling effects on the cationic ordering and electrochemical properties
  - local oxidation process of Ni *vs* Mn/Co within single particles
  - morphology control through tuning synthesis conditions
- Develop new techniques/capabilities for probing synthesis
  - *in-situ* solvothermal synthesis with *real time* monitoring of synthesis parameters (P, T, pH values)
  - *in-situ* neutron, synchrotron techniques for both bulk and local studies
- Apply the established approaches/techniques to synthesis of other types of high-capacity cathode (*i.e. Li-rich disordered cathodes, spinel-layered composite cathodes*), *via* collaboration within BMR and with external partners.

Any proposed future work is subject to change based on funding levels

Summary

We have established techniques/approaches for preparing high-performance Ni-rich layered oxide cathodes through synthetic control of the structural ordering in electrode materials.

- **Relevance:** Develop low-cost, high energy density cathode with electrochemical properties consistent with USABC goals.
- **Approaches:** *in-situ* techniques were developed, enabling us to
  - identify reaction pathways/intermediates in preparation of cathode materials
  - quantify thermodynamic and kinetic parameters governing synthesis process
- **Technical Accomplishments:** Synthesis procedures were developed for making a series of Ni-rich layered oxides W/ demonstrated high reversible capacity: $LiNi_{1-x}Co_xO_2$, $LiNi_{0.7}(CoMn)_xO_2$
- **Collaborative Research:** Established extensive collaborations within BMR and W/ external partners on synthesis/characterization of cathodes.
- **Future Work:** Explore the impact of synthesis parameters on the structure and electrochemical properties of Ni-rich layered oxides and other high-capacity cathodes, through *in-situ* studies.

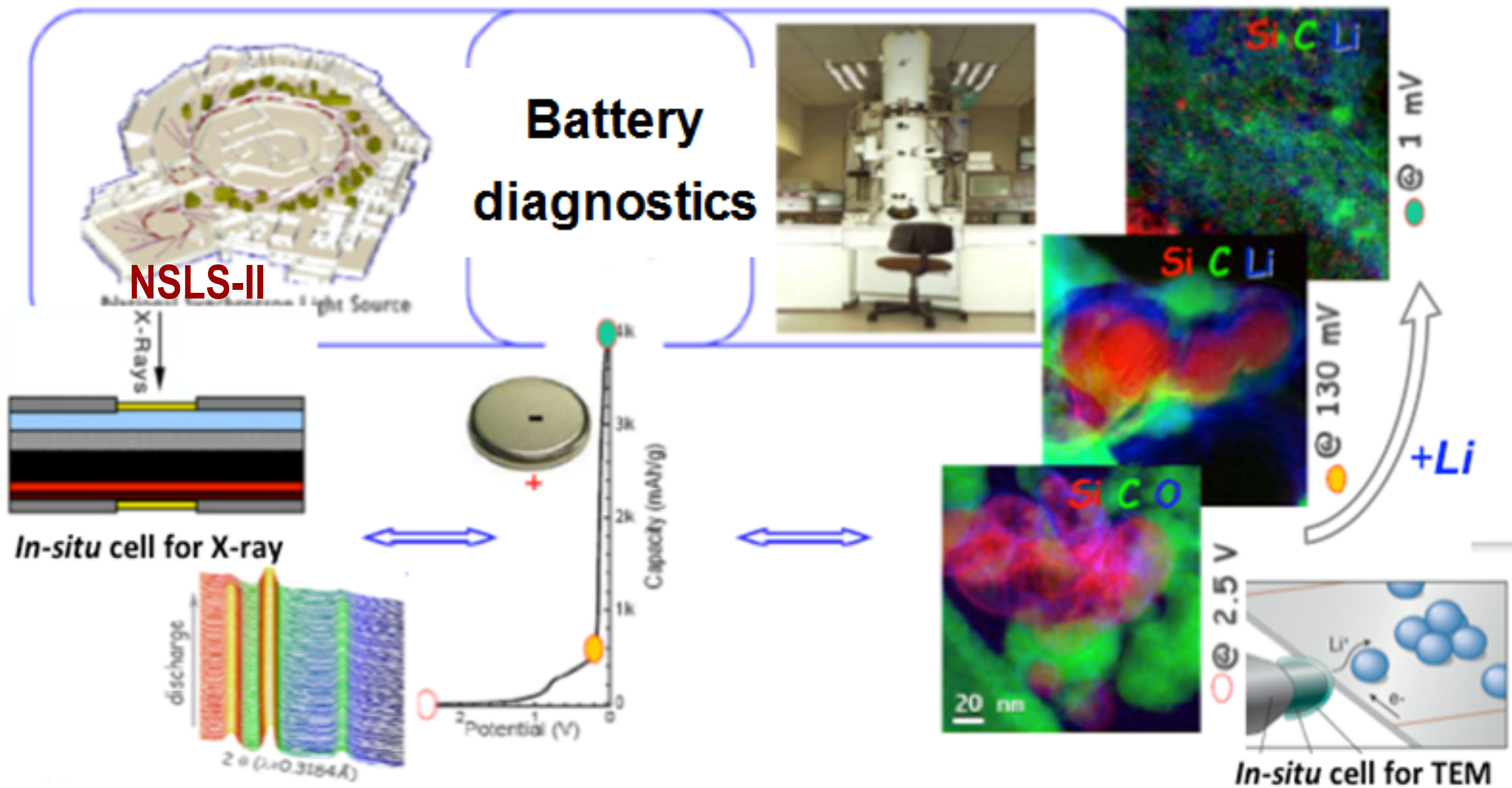
Any proposed future work is subject to change based on funding levels

Acknowledgement

- Support from the BMR Program, Office of Vehicle Technologies, DOE-EERE, is gratefully acknowledged (Program Manager: Tien Duong)
- Team members: Mingjian Zhang, Hu Zhao, J. Patrick Looney

Technical Backup Slides

Backup (1): Diagnostics Using *on-site* Resources and *in-house* Developed Capabilities



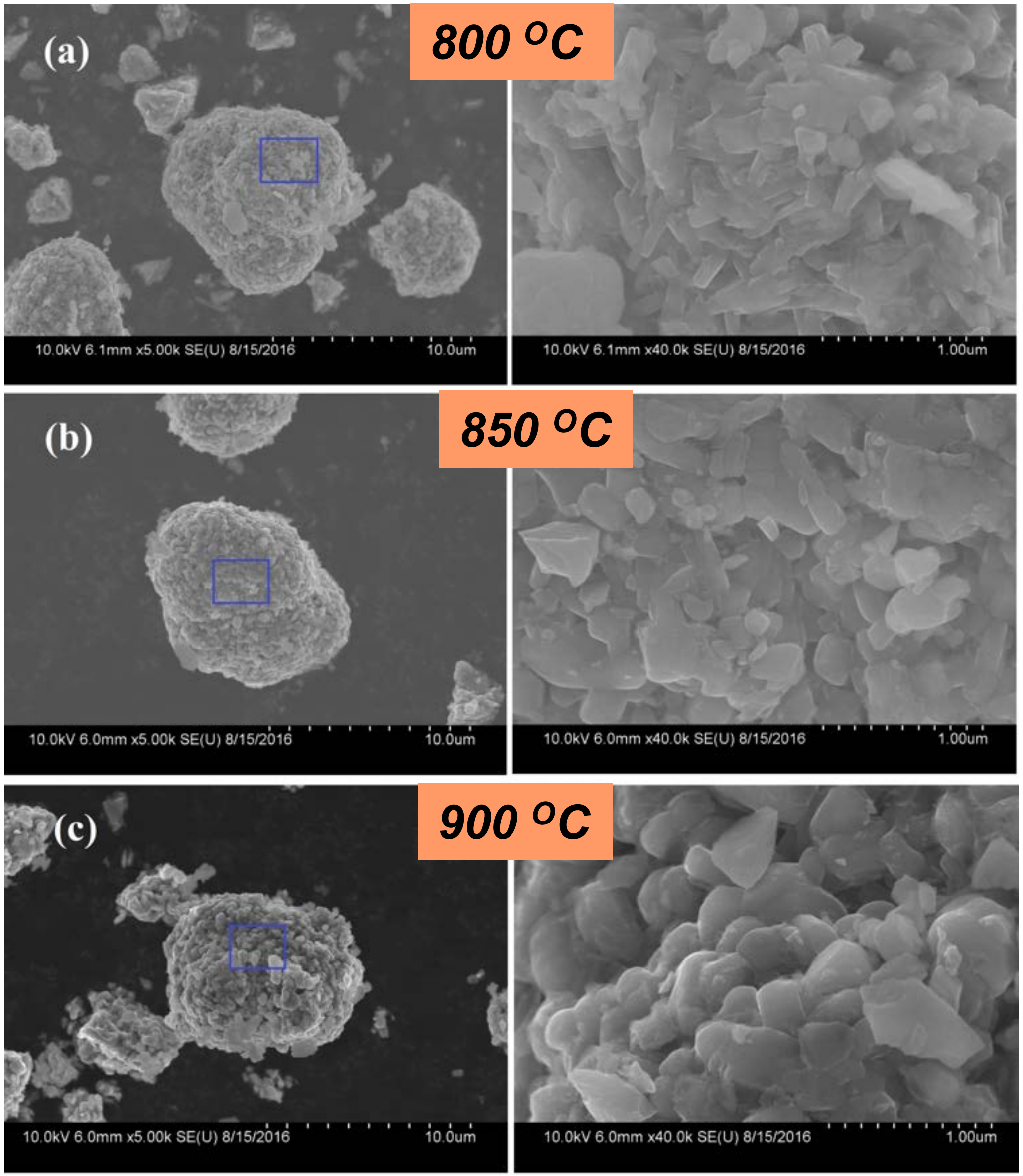
Synchrotron x-ray
studies of Li reaction, charge transfer @ electrode level.

Electrochemistry
(*Functionality*)

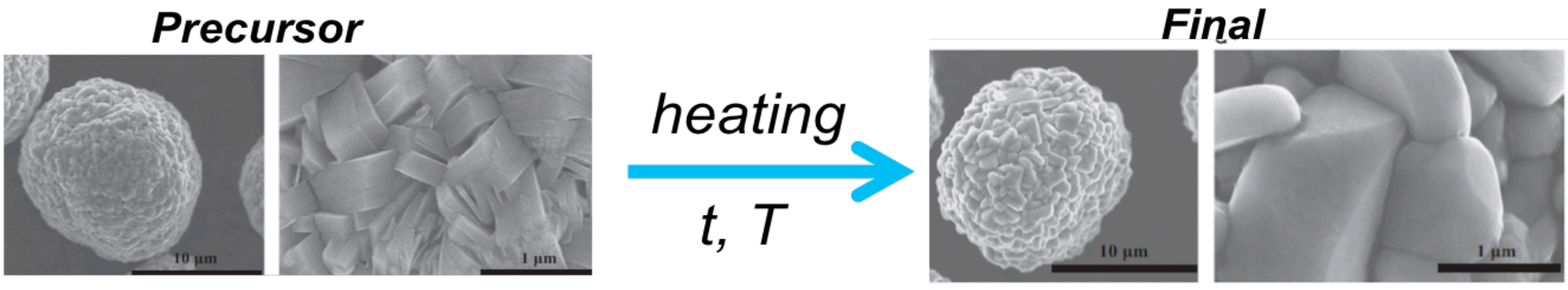
TEM-EELS
tracking Li transport, reactions *@single-particle level.*

*__Ref.__: F. Wang et al., *Adv. Energy Mater.* 3 (2013) 1324; *Nat. Comm.*, 3 (2012)120 & 6 (2015) 6668.

Backup (2): Morphology of the synthesized NMC71515 at different temperatures

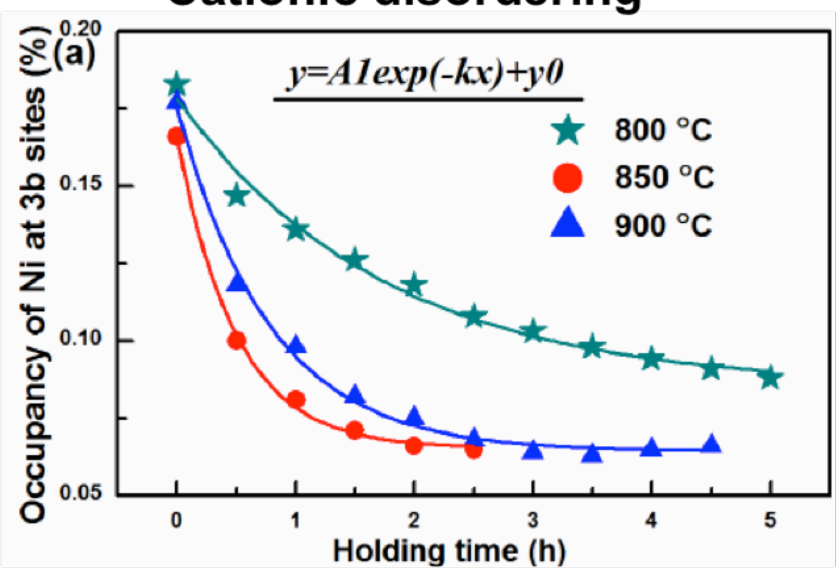


Backup (3) Synthetic control of the morphology through tuning synthesis conditions (**based on in-situ XRD studies*)



Li et al., Nano Energy (2016)

Cationic disordering



Particle size